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(21) International Application Number: PCT/GB99/00427 (22) International Filing Date: 11 February 1999 (11.02.99) (30) Priority Data: 9804143.7 26 February 1998 (26.02.98) GB (71) Applicant (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BONNER, James, Graham [GB/GB]; 29 Connaught Place, Edinburgh EH6 4RQ (GB). POWELL, Anthony, Keith [GB/GB]; 75 Abalon Gardens, Linlithgow Bridge, Linlithgow EH49 7PL (GB). (74) Agent: COLLINS, Frances, Mary; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A MULTI-LAYERED STRUCTURE (57) Abstract A multi-layered structure comprising a first polyolefin or styrenic polymer layer and a second polyketone layer, the first and second layers being bonded together with an intermediate layer of an adhesive blend comprising (A) a graft copolymer having a polyolefin or a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof; (B) a polyamide; and (C) optionally a polyolefin.		

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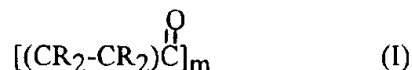
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A MULTI-LAYERED STRUCTURE

The present invention relates to adhesive blends and multi-layered structures comprising the adhesive blends, in particular, multi-layered structures comprising at least one layer of a polyketone composition.

For the purposes of this patent, polyketones are defined as linear
5 polymers having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds. Although for the purposes of this patent polyketones correspond to this idealised structure, it is envisaged that materials corresponding to this structure in the main but containing small regimes (i.e. up to 10wt%) of the corresponding
10 homopolymer or copolymer derived from the olefinically unsaturated compound, also fall within the definition.

Such polyketones have the formula:



15 where the R groups are independently hydrogen or hydrocarbyl groups, and m is a large integer; they are disclosed in several patents e.g. US 3694412. Processes for preparing the polyketones are disclosed in US 3694412 and also in EP 181014 and EP 121965.

Adhesive compositions, also known as tie-layers or melt adhesives, are
20 employed to bind together layers of materials which otherwise do not stick together satisfactorily. Polyolefin-containing blends suitable for use as adhesive layers in multi-layered structures are known. For example, US Patent 2081723 discloses a modified polyolefin adhesive blend comprising (A) a graft copolymer of a polyethylene back-bone grafted with at least one polymerisable ethylenically
25 unsaturated carboxylic acid or carboxylic acid anhydride and (B) a blending resin

mixture comprising a linear low density polyethylene and polypropylene. The patent states that the adhesive blends can be used to join polypropylene to a number of polar materials or to join two polar materials together.

WO 9509212 relates to a polyolefin-containing adhesive blend comprising:

- 5 (A) 1 to 30 parts by weight of a graft copolymer having a polyolefin backbone grafted with 0.001 to 30% by weight of at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof,
- (B) 70 to 99 parts by weight of a polyolefin provided that at least 5 parts by weight of (B) is
- 10 (C) a polyolefin having a density of less than 930kgm^{-3} wherein the graft copolymer (A) has been reacted with a compound (D) which has at least two primary or secondary amino groups at least one of which is a primary amino group, the sum of (A), (B) and (C) being 100 parts by weight. The polyolefin-containing adhesive blend of WO 9509212 is said to be suitable for
- 15 bonding polyolefins in particular polyethylene or polypropylene to polyketones and has good adhesion to polyolefins while maintaining good adhesion to the polyketone.

There remains the need for further adhesive blends which have good adhesion to polyketones.

- 20 Thus, according to the present invention there is provided a multi-layered structure comprising a first layer and a second layer, the first layer comprising a polyolefin or styrenic polymer composition and the second layer comprising a polyketone composition, the first and second layers being bonded together with an intermediate layer of an adhesive blend comprising:

- 25 (A) a graft copolymer having a polyolefin or a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof;
- (B) a polyamide; and
- (C) optionally a polyolefin.

- 30 The polymer used as the backbone of the graft copolymer (A) can be a homopolymer of an olefin e.g. ethylene or propylene, in particular high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) or very low density polyethylene (VLDPE), preferably LLDPE, or a copolymer of an olefin e.g. propylene with ethylene, butene or other
- 35 unsaturated aliphatic hydrocarbons. Such homopolymers and copolymers are

known and any such polymer can be used. Blends of two or more polyolefins can be used. It is preferred that the backbone of (A) is polypropylene or polyethylene. Where the polyolefin backbone is a copolymer it is preferred that it comprises at least 80% of polymerised ethylene or 80% of polymerised propylene units. Where
5 the adhesive blend is used to bond a polyolefin to a polyketone, it is preferred that the polyolefin used in the backbone of (A) is the same as the polyolefin to be bonded. For example when polypropylene is to be bonded to polyketone by means of the adhesive blend, component (A) is a graft copolymer of polypropylene.

The polymer used as the backbone of the graft copolymer (A) can also be
10 a styrenic polymer. The styrenic polymer may be a copolymer of a vinyl aromatic hydrocarbon (e.g. styrene or substituted styrenes such as α -methyl styrene, α -ethylstyrene, p-methylstyrene, m-methylstyrene, p-ethylstyrene, m-isopropylstyrene, divinyl benzene, α ,4-dimethylstyrene, chlorostyrene and vinyl benzene chloride) with an ethylenically unsaturated comonomer other than a vinyl
15 aromatic hydrocarbon and optionally a diene (e.g. butadiene, ethylidene norbornene). Suitable ethylenically unsaturated comonomers are given in "Polymer Handbook" by J Brandrup and E H Immergut, 3rd Edition, (1989), Section II, pages 214-248, Wiley - Interscience publication. Preferably, the ethylenically unsaturated comonomer is maleic anhydride or methyl methacrylate. For example,
20 the styrenic polymer may be a copolymer of styrene with maleic anhydride (SMA), a terpolymer of styrene, maleic anhydride and butadiene, a copolymer of styrene with methyl methacrylate or a terpolymer of styrene, methyl methacrylate and maleic anhydride. Typically, the styrenic polymer is a copolymer of styrene with maleic anhydride wherein the copolymer has up to 50%, preferably 5 to 20%, more
25 preferably 9 to 14% by weight of units derived from maleic anhydride along the polymer backbone or is a terpolymer of styrene, maleic anhydride and butadiene wherein the terpolymer has 5 to 20% by weight of units derived from maleic anhydride and 5 to 20% by weight of units derived from butadiene along the polymer backbone, preferably about 10 and 13% by weight of units derived from
30 maleic anhydride and butadiene respectively. These preferred materials are sold by Nova Chemicals under the trade name of DYLARK or by Bayer under the trade name of Cadon. Alternatively, styrenic block copolymers may be employed. The term "styrenic block copolymer" is used to indicate a thermoplastic elastomer characterised by at least one block of units derived from a vinyl aromatic
35 hydrocarbon (A block) and at least one block of units derived from one or more

olefins other than a vinyl aromatic hydrocarbon (B block). The vinyl aromatic hydrocarbon useful as the precursor of A blocks has a vinyl group attached directly to an aromatic ring. Preferred vinyl aromatic compounds are styrene and substituted styrenes. Illustrative substituted styrenes are as listed above. Olefins
5 useful as precursors of the B blocks include ethylene, propylene, butylene, and dienes (e.g. isoprene, butadiene 2,3-dimethylbutadiene, 1,3-octadiene, 1,3-pentadiene and norbornene). Preferably the styrenic block copolymer has the structure A-B-A. Examples of styrenic block copolymers include styrene-ethylene/butylene-styrene block terpolymer (SEBS), styrene-butadiene-styrene
10 terpolymer (SBS) and styrene-isoprene-styrene terpolymer (SIS). These styrenic block copolymers are sold by Shell under the trade name of Kraton and by Asahi under the trade name of Tuftec. Blends of two or more styrenic polymers can be used. Where the adhesive blend is used to bond a styrenic polymer to a polyketone, it is preferred that the styrenic polymer used in the backbone of
15 component (A) of the adhesive blend is the same as the styrenic polymer to be bonded.

Polymerisable ethylenically unsaturated carboxylic acids and derivatives thereof include, for example, acrylic acid, methacrylic acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, maleic anhydride, 4-methyl cyclohex-4-ene-
20 1,2-dicarboxylic acid anhydride, bicyclo (2.2.2) oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3 dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro (4.4) non-7-ene, bicyclo (2.2.1) hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, x-methyl-bicyclo (2.2.1) hept-5-ene -2,3-dicarboxylic acid anhydride, x-methyl-norborn-5-ene-2,
25 dicarboxylic acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride. Preferably, maleic anhydride is used. When maleic anhydride is used as the polymerisable ethylenically unsaturated carboxylic acid anhydride, the amount which is graft copolymerised with a polyolefin backbone is typically from 0.001 to 30%, preferably from 0.1 to 10% more preferably from 0.15 to 5 % by weight of
30 the grafted copolymer. The amount of maleic anhydride which is graft copolymerised with a styrenic polymer backbone is typically from 0.001 to 5%, preferably from 0.05 to 3% more preferably from 0.5 to 2 % by weight of the grafted copolymer.

Co-grafting monomers such as, for example, those described in US Patent
35 3882194 may also be used for preparing the graft copolymers of the present

invention.

Component (A) of the blend of the present invention may comprise a mixture of two or more graft copolymers e.g. a mixture of a graft copolymer having a polyolefin backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof and a graft copolymer having a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof.

Methods for preparing graft copolymers are well known and any suitable method can be used to prepare the graft copolymer of the polyolefin or styrenic polymer and the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof. One such suitable method comprises blending together the polyolefin or the styrenic polymer and the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof in the presence of a free radical initiator, such as an organic peroxide or hydroperoxide, at a temperature which is above the melting point of the polyolefin or the styrenic polymer and which provides a suitable half-life of the free radical initiator. Suitable free radical initiators are well known. This grafting process can be carried out using known mixing equipment such as, for example, a Brabender mixer, a Banbury mixer or a roll mill. Preferably, the grafting process is carried out in a closed vessel. A convenient method of preparing the graft copolymer is therefore to extrude the polyolefin or the styrenic polymer which forms the polymer backbone, the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof and an organic peroxide or hydroperoxide through a single or multiple screw extruder. Alternatively, the polyolefin or styrenic polymer which forms the polymer backbone may be dissolved or suspended in a solvent and the resulting solution or suspension is mixed with the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof and the free radical initiator.

The graft copolymer (A) may be present in the adhesive blend in amounts of from 1 to 99 % by weight, preferably 5 to 50 % by weight, based on the total amount of the blend.

Turning to component (B) of the adhesive blend, by the term "polyamide" is meant a condensation product which contains recurring amide groups as integral parts of a polymeric chain. These polyamides are well known in the art and are often referred to as Nylons.

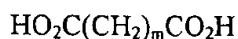
The polyamide may be a homopolymer of an aminomonocarboxylic acid,

typically having up to 16 carbon atoms inclusive, for example, Nylon 12 or Nylon 6. Alternatively, the polyamide may be a copolymer of a primary diamine and a dicarboxylic acid. The primary diamine is preferably a terminal primary diamine having up to 16 carbon atoms inclusive and at least two carbon atoms between the
5 primary amino groups which are located on terminal carbon atoms of the diamine structure. The diamines suitably contain aromatic moieties linking the amino groups as illustrated by phenylenediamine, 4,4'-diaminobiphenyl and di(4-aminophenyl)ether, or the linking group is cycloaliphatic as in the case of di(4-aminocyclohexyl)methane or 1,4-diaminocyclooctane. The preferred diamines,
10 however, are acyclic terminal primary diamines of the formula:



wherein n is an integer from 2 to 16 inclusive. Such polymethylenediamines
15 include trimethylenediamine, tetramethylenediamine, hexamethylenediamine, decamethylenediamine, dodecamethylenediamine and hexadecamethylenediamine.

The dicarboxylic acid suitably has up to 16 carbon atoms inclusive as illustrated by aromatic dicarboxylic acids such as isophthalic acid, terephthalic acid and 2,6-naphthalenedicarboxylic acid. The preferred dicarboxylic acids, however,
20 are aliphatic dicarboxylic acids, particularly those of the formula



wherein m is an integer from 0 to 14 inclusive. Illustrative of such dicarboxylic
25 acids are oxalic acid, pimelic acid, sebacic acid, suberic acid, azelaic acid, undecanedioic acid, and adipic acid.

The molecular weight of the polyamide is preferably at least 5,000, most preferably in the range 5,000 to 250,000.

Component (B) of the adhesive blend may comprise a mixture of two or
30 more polyamides.

The polyamide may be present in the adhesive blend in amounts of from 5 to 90% by weight, preferably 15 to 70% by weight, typically 25 to 50% by weight, based on the total amount of the adhesive blend.

Optional component (C) of the adhesive blend can be any suitable
35 polyolefin e.g. polyethylene, polypropylene, copolymers of ethylene or copolymers

of propylene with one or more comonomers e.g. butene. Typically, component (C) may be a very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE) or an ethylene propylene rubber. Component (C) may comprise more than one polyolefin, preferably two polyolefins e.g. a polypropylene and a VLDPE.

5 Optional component (C) is added to modify the rheological, viscoelastic or adhesive properties of the adhesive blend.

Where component (C) is present in the adhesive blend, the polyolefin is present in amounts of from 5 to 95% by weight, preferably 5 to 25 % by weight, based on the total amount of the adhesive blend.

10 The adhesive blend may optionally comprise a polyketone. Where a polyketone is present in the adhesive blend it is preferred that the polyketone is present in the adhesive blend in amounts in the range 10 to 50% by weight, more preferably 20 to 40% by weight based on the total amount of the adhesive blend.

15 The adhesive blends comprising (A) the graft copolymer, (B) the polyamide, (C) the optional polyolefin and further comprising an optional polyketone can be prepared using known techniques and equipment for batch or continuous blending.

20 The adhesive blends may also contain additives conventionally used in such blends such as, for example, antioxidants, stabilisers, processing aids, fillers and mould release agents.

25 It is to be understood that when in the specification and claims herein, the amounts of components (A), (B) or (C) and of the optional polyketone are expressed in terms of percent by weight, it is meant, unless otherwise indicated, percent by weight based on the total weight of the adhesive blend, excluding further components.

30 Methods for using adhesive blends to bond polyolefins or styrenic polymers to polar substrates are known and include lamination, coextrusion, extrusion lamination and coextrusion coating. In particular, the present invention relates to multi-layered structures when prepared by co-extrusion e.g. multi-layered film, multi-layered sheet, multi-layered receptacles (such as bottles, cups, bowls and trays), multi-layered pipe and multi-layered tubing produced by co-extrusion.

35 Where the first layer comprises a polyolefin composition, the polyolefin composition can be a polyolefin, blends of polyolefins or blends of a polyolefin and a polymer other than a polyolefin (for example, a blend of a polyolefin and a polyamide). Preferably, the polyolefin composition of the first layer comprises a

major proportion of a polyolefin. The polyolefin composition of the first layer may comprise a recycled polyolefin or a mixture of recycled and virgin polyolefin. The polyolefin composition of the first layer may contain conventional fillers. Suitable polyolefins include a homopolymer of an olefin e.g. ethylene or propylene, in particular polypropylene, a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE) or a very low density polyethylene (VLDPE), preferably polypropylene, HDPE or LLDPE. Alternatively, the polyolefin may be a copolymer of an olefin e.g. propylene with ethylene, butylene or other unsaturated aliphatic hydrocarbons or a terpolymer of an olefin e.g. ethylene with propylene and a diene.

Where the first layer comprises a styrenic polymer composition, the styrenic polymer composition can be a styrenic polymer as defined above, blends of styrenic polymers or blends of a styrenic polymer and a polymer other than a styrenic polymer. The polymer composition of the first layer may contain conventional fillers.

The polyketone composition of the second layer comprises a linear polymer having an alternative structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds. Suitable olefinic units are those derived from C_2 to C_{12} alpha-olefins or substituted derivatives thereof or styrene or alkyl substituted derivatives of styrene. It is preferred that such olefin or olefins are selected from C_2 to C_6 normal (straight chain) alpha-olefins and it is particularly preferred that the olefin units are either derived from ethylene or most preferred of all from a mixture of ethylene and one or more C_3 to C_6 normal alpha-olefin(s) especially propylene or butylene. In these most preferable materials it is further preferred that the molar ratio of ethylene units to C_3 to C_6 normal alpha-olefin units is greater than or equal to 1 most preferably between 2 and 30. The polyketone composition of the second layer may comprise blends of polyketones or blends of polyketones and a polymer other than a polyketone (for example, polystyrene, polyamides, HDPE, LLDPE, LDPE or polypropylene).

The polyketones employed in the invention preferably have a number average molecular weight of from 20000 to 500,000, preferably from 30,000 to 300,000, more preferably from 40,000 to 200,000 as determined by gel permeation chromatography.

The melting point of the polyketones is preferably between 175 and 300°C,

preferably from 180 to 260°C.

The multi-layered structures according to the present invention can include further layers in addition to the three layers hereinbefore defined. For example, a five-layered structure can comprise a first layer of a polyolefin or styrenic polymer composition, a second layer of an adhesive blend as defined
5 above, a third layer of a polyketone composition, a fourth layer of an adhesive blend as defined above and a fifth layer of a polyolefin or styrenic polymer composition.

It has been found that the use of the adhesive blends defined above to
10 produce multi-layered film or sheet provides a satisfactory bond when the film or sheet is subsequently thermoformed, i.e. the film or sheet does not have a tendency to delaminate after thermoforming into articles, e.g. into receptacles (such as bottles, bowls, cups or trays), pipes and tubing. The present invention includes articles produced by thermoforming a multi-layered film or sheet as previously
15 defined.

The invention is illustrated by the following example:

Materials

Polyketone (PK): Ethylene/propene/CO terpolymer, melting point 200°C, melt flow rate (MFR) 70 g/10 minutes (250°C, 5 kg load).

20 Polyamide 12 (PA12): L1700 supplied by Huls UK Limited;

Maleic anhydride grafted ethylene-propylene rubber (MAH-g-EP):
Exxcelor VA1801 supplied by Exxon;

EP (ethylene-propylene rubber): Exxcelor PE 805 supplied by Exxon
Chemical Limited.

25 Polyethylene (PE): LL0209 supplied by BP Chemicals Limited.

Determination of Melt Flow Rate

The melt flow rate (MFR) of the polyketone (PK) was measured using a Davenport Melt Index Tester. Tests were carried out at a temperature of 250°C and an applied load of 5 kg. The MFR was calculated from the mass of extrudate
30 pushed through a die (2.095 mm diameter) over a 30 second period on application of the load 4 minutes after charging the polymer into the barrel of the instrument at a temperature of 250°C. Otherwise, standard MFR procedures were followed (e.g. ISO 1133).

Example

35 Blends of 70/30 PA12/MAH-g-EP and 70/30 PA12/EP were produced via

melt extrusion using a PRISM 16 mm co-rotational twin screw extruder.

Compression moulded sheets (150 μ m) of each blend were produced using a 20 tonne Moore press under the following conditions: a 15 x 15 cm x 130 μ m "picture frame" mould was preheated for 5 minutes at 200°C, pressed at 15 tonnes for 5 minutes and crash cooled to room temperature.

Polyketone (PK) and polyethylene (PE) sheets were made by a similar procedure to that given above.

Multi-layered structures of PK/blend/PE were prepared via the following procedure: three individual sheets (PK/blend/PE) were placed within a 15 x 15 cm x 390 μ m picture frame mould. This was preheated at 260°C for 30 seconds, pressed at 10 tonnes for 10 seconds and then crash cooled to room temperature. The resultant multi-layered structure was then cut into five 2.5 cm wide strips and the level of adhesion between each layer was assessed using a standard T-peel test (in accordance with BS 5350).

The PA12/MAH-g-EP blend could not be peeled from either the polyketone (PK) or polyethylene (PE) layers of the multi-layered structure. However, PA12/PE blend was easily peeled away from the polyethylene (PE) layer.

Claims:

1. A multi-layered structure comprising a first layer and a second layer, the first layer comprising a polyolefin or styrenic polymer composition and the second layer comprising a polyketone composition, the first and second layers being bonded together with an intermediate layer of an adhesive blend comprising:
 - 5 (A) a graft copolymer having a polyolefin or a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof;
 - (B) a polyamide; and
 - (C) optionally a polyolefin.
- 10 2. A multi-layered structure as claimed in claim 1 wherein the polymer used as the backbone of the graft copolymer (A) is polypropylene or polyethylene.
3. A multi-layered structure as claimed in claim 1 wherein the polymer used as the backbone of the graft copolymer (A) is selected from the group consisting of a copolymer of styrene with maleic anhydride (SMA), a terpolymer of styrene,
 - 15 maleic anhydride and butadiene, a copolymer of styrene with methyl methacrylate, and a terpolymer of styrene, methyl methacrylate and maleic anhydride.
4. A multi-layered structure as claimed in claim 1 wherein the polymer used as the backbone of the graft copolymer (A) is a block copolymer having at least one block of units derived from a vinyl aromatic hydrocarbon (A block) and at
 - 20 least one block of units derived from one or more olefins other than a vinyl aromatic hydrocarbon (B block).
5. A multi-layered structure as claimed in any one of the preceding claims wherein the graft copolymer (A) is present in the adhesive blend in amounts of from 5 to 50 % by weight based on the total amount of the blend.
- 25 6. A multi-layered structure as claimed in any one of the preceding claims

wherein component (B) of the adhesive blend is a homopolymer of an aminomonocarboxylic acid, typically having up to 16 carbon atoms inclusive or a copolymer of a primary diamine and a dicarboxylic acid.

7. A multi-layered structure as claimed in any one of the preceding claims
5 wherein the polyamide is present in the adhesive blend in amounts of from 15 to 70% by weight based on the total amount of the adhesive blend.

8. A multi-layered structure as claimed in any one of the preceding claims wherein component (C) is present in the adhesive blend in an amount of from 5 to 25 % by weight based on the total amount of the adhesive blend.

10 9. A multi-layered structure as claimed in any one of the preceding claims wherein the adhesive composition further comprises a polyketone in an amount in the range 10 to 50% by weight based on the total amount of the adhesive blend.

10. A multi-layered structure as claimed in any one of the preceding claims wherein the polyketone composition of the second layer comprises a linear polymer
15 having an alternative structure of (a) units derived from carbon monoxide and (b) units derived from ethylene and one or more C₃ to C₆ normal alpha-olefins.

11. A multi-layered structure as claimed in any one of the preceding claims wherein the multi-layered structure comprises a first layer of a polyolefin or styrenic polymer composition, a second layer of the adhesive blend, a third layer of
20 a polyketone composition, a fourth layer of the adhesive blend and a fifth layer of a polyolefin or styrenic polymer composition.

12. An article comprising a multi-layered structure as claimed in any one of the preceding claims.

13. An article as claimed in claim 12 wherein the article is selected from the
25 group consisting of receptacles, pipe or tubing.

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/GB 99/00427

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 C08L51/06 C08L77/00 C09J177/00

According to international Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B C08L C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 637 410 A (BONNER JAMES G ET AL) 10 June 1997	1,2,5,6, 11-13
Y	see claims 1-4,10-12,17,20	3,4,7,8 10
A	---	
Y	EP 0 703 279 A (BUNA SOW LEUNA OLEFINVERB GMBH) 27 March 1996	1-8, 11-13
	see claims 1-4	
A	---	
	DE 35 04 696 A (TAKEDA CHEMICAL INDUSTRIES LTD) 14 August 1985	1,5,7,8, 12,13
	see the whole document	

☐ Further documents are listed in the continuation of box C.

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